



A comparative investigation into the formation behaviors of char, liquids and gases during pyrolysis of pinewood and lignocellulosic components



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HIGHLIGHTS

- Lignin accelerated the decomposition of cellulose.
- Complex componential interactions occurred during pine wood pyrolysis.
- Pine wood-derived char was more inhomogeneous in the constituents.
- Pine wood produced more bio-oil than xylan, cellulose and ADF.
- ADF- and pine wood-derived bio-oils were less oxygenated.

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ABSTRACT

The pyrolysis characteristics of xylan, cellulose, ADF (a mixture of cellulose and lignin extracted from pine wood) and pine wood were investigated in a fixed-bed reactor by determining the distributions of three-phase products, the elemental compositions of char products, the conversions of components and the profiles of gas release rate during pyrolysis as well as the compositions of liquid products. Interactions were found to occur between the different components. Lignin accelerated the release of CO₂ and CO from cellulose and intensified the decomposition of cellulose to smaller molecular weight liquid compounds. Pine wood exhibited the componential interactions, resulting in the broadened temperature range of mass loss, the enhanced yield of char, and the increased heterogeneity of char. Pine wood produced more bio-oil than each component sample, with the compositional formula of CH_{1.07}O_{0.31}. The formation of liquid compounds from pine wood was also observed to be influenced by the componential interactions.

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1. Introduction

Biomass as a renewable and carbon-neutral energy resource has recently received a considerable interest over the world. Many advanced technologies are being vigorously developed to modernize the inherited and laggard patterns of biomass utilization (Mohammad et al., 2012). Pyrolysis is an important thermochemical conversion process, which is promising particularly for the conversion of lignocellulosic biomass to solid product (bio-char), liquid product (bio-oil), and gaseous product. The pyrolysis products become more energy-intensive and easier to transport and handle, and thus are more useful and more efficient in use. Moreover, the pyrolysis process is versatile to optimize three-phase products in their yields and properties for match with downstream

processing to a wide range of value-added products, such as transportation fuels and fine chemicals.

On the other hand, biomass pyrolysis is a complex process involving in almost innumerable reactions of degradation, depolymerization, decomposition, recombination, isomerization, repolymerization and condensation occurring in both fixed phase (solid) and dynamic phase (gas and liquid). The pyrolysis behaviors are influenced by a multitude of conditional parameters, such as heating rate, final temperature, residence time and catalyst (Mythili et al., 2013; Pasangulapati et al., 2012; Stefanidis et al., 2014; Wang et al., 2013, 2009). The complexity is also due to the compositional diversity of biomass (Sanchez-Silva et al., 2012). In general, lignocellulosic biomass is composed of three main components (hemicellulose, cellulose and lignin), with some extractives. The different pyrolysis characteristics of individual components in company with their interactions lead to multivariable scenarios in the distributions, compositions and properties of products. To design an efficient biomass thermoconversion process toward the

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production of desired products, it is essential to understand the pyrolysis behaviors of individual components and their interactions.

Numerous researches have addressed the pyrolysis characteristics of hemicellulose, cellulose and lignin. One aspect is the thermal stability of three components (Cao et al., 2014; Lv et al., 2013; Raveendran et al., 1996; Shen and Gu, 2009; Yang et al., 2007). Hemicellulose is a polysaccharide consisting of pentose and hexose monomers (e.g., xylose, galactose, mannose, and arabinose) and their acidified forms (e.g., glucuronic acid and galacturonic acid). It is affirmed to be a labile component due to its amorphous structure unlike crystalline cellulose (Ebringerová et al., 1992; Peng and Wu, 2010). Lignin, a cross-linked polymer of aromatic alcohols, contains thermally unstable and resistant functional groups so that the decomposition covers a wide range of temperature (Lv et al., 2013; Yang et al., 2007). A more important aspect is the distributions and compositions of three-phase products from individual components. Lignin is known as a good precursor of char production, while cellulose is highly volatile (Raveendran et al., 1996; Wang et al., 2011). The release profiles and productivities of gases (H_2 , CO_2 , CO , CH_4 , etc.) from individual components have been extensively investigated using TG–FTIR and fixed-bed reactor (Shen and Gu, 2009; Xin et al., 2013; Yang et al., 2007). Yang et al. (2007) reported that hemicellulose (xylan) had higher CO_2 yield, cellulose generated higher CO yield, and lignin owned higher H_2 and CH_4 yield. To understand the reaction pathways and mechanism of biomass pyrolysis, researchers have devoted to characterizing the compositions of bio-oils derived from individual components. Acids, furans and ketones are the typical liquid compounds formed from hemicellulose in the case of less severity of secondary pyrolysis (Shen et al., 2010). Levoglucosan is an initial product degraded from cellulose, and it can be subsequently cracked to low molecular weight volatiles (Brandbury et al., 1979; Pasangulapati et al., 2012). Guaiacols and phenols are mainly ascribed to the breakage of lignin (Stefanidis et al., 2014). However, a bio-oil produced from even a single component generally contains copious oxygenated compounds depending on pyrolysis conditions. This makes it difficult to quantitatively determine all compounds in bio-oil.

There is a rationale that the pyrolysis of a biomass holds an additive result if the interactions of components in it can be ignored. Raveendran et al. (1996) argued from the mass loss profiles and the product distributions that there was no noticeable interaction between the components during pyrolysis in both the TGA and the packed bed reactor. Stefanidis et al. (2014) observed on the TGA that the final char yields of the component mixture could be predicted from those of individual components in an additive way, but the DTG curves displayed limited heat transfer when using the mixing sample. In recent years, however, several studies have justified the interactions between different components from the yields of liquid compounds. Hosoya et al. (2007, 2009) found that lignin suppressed the polymerization of cellulose-derived levoglucosan and accelerated the gas formation; cellulose in turn reduced the char formation of lignin along with more production of lignin-derived liquids such as guaiacols. While Hosoya et al. observed weak interaction between cellulose and hemicellulose, some studies indicated the inhibitory effect of hemicellulose on the formation of altrose and levoglucosan from cellulose and the cellulose-promoted formation of hemicellulose-derived acetic acid and furfural (Liu et al., 2011; Wang et al., 2011).

In this work, a special effort is made to quantify the yields and compositions of all three-phase products in a unified experiment, for a better understanding of the relationships between the formations of three-phase products and the elemental partitions to three-phase products. Since the commercial reagent of lignin is commonly alkalinized or acidified, which is likely to be much

different in nature with lignin in pine wood, a specific sample of cellulose and lignin mixture (ADF) isolated gently from pine wood is used in the study. Comparison has therefore been made between biomass components and pine wood to correlate their pyrolysis characteristics and to reveal the interactions between different components. Moreover, the conversions of different components during pyrolysis are examined by an extraction method.

2. Experimental

2.1. Materials

The pine wood sample was the sawdust waste collected from a local wood processing factory in Shanghai, China. The pine wood sample was sieved to the particle size of about 0.15–0.45 mm. The pine wood sample used in all experiments was dried at 105 °C to a constant weight. The samples of cellulose and xylan were purchased from Aladdin Ind. Co. The cellulose sample was a white powder with the particles size of around 0.19 mm. The xylan sample was a white powder with the particle size of less than 0.15 mm. From the sample instruction, the xylan sample was separated from birch wood. The sample of a mixture of cellulose and lignin (ADF) was obtained by complete removal of extractives and hemicellulose from the pine wood sample used. The extraction method is described in the next section. The proximate and ultimate analyses of the four samples (pine wood, cellulose, xylan, and ADF) are shown in Table 1. The contents of main components in the four samples are shown in Table 2. It should be pointed out that xylan, although generally a representative sample of hemicellulose, behaves unlike hemicellulose in the solubility. The xylan sample is entirely soluble in an aqueous solution of sodium lauryl sulfate like a neutral detergent solute (NDS), whereas hemicellulose inherent in biomass is classified to be insoluble in this solution.

2.2. Determination of fiber components

A national standard method of China (GBT-20805-2006) was used to determine the main components in the four samples used in this study. This method is widely applied to determine the fiber constituents in various vegetable feeds such as forages and food-stuffs. In this method, a biomass is divided into four main components, neutral detergent solute (NDS), hemicellulose, cellulose, lignin, with residual ash (silicate). The main procedures are described elsewhere (Shi et al., 2012) and outlined as follows.

A segment of biomass sample is used to extract out NDS by refluxing in a neutral detergent (3% sodium lauryl sulfate). The extractive (NDS) is typically composed of saccharide, starch, fat and various nutrients (protein, terpene, etc.). The insoluble remainder obtained after removal of NDS is termed neutral detergent fiber

Table 1
Properties of biomass samples.

	Xylan	Cellulose	ADF	Pine wood
<i>Proximate analysis (wt.%, dry basis)</i>				
Volatile	93.6	93.9	78.5	87.2
Fixed carbon ^a	6.3	6.1	21.1	12.3
Ash	0.1	–	0.4	0.5
<i>Ultimate analysis (wt.%, daf. basis)</i>				
C	43.9	44.3	52.5	51.8
H	6.4	6.2	6.4	6.3
O ^a	49.5	49.5	40.8	41.7
N	–	–	0.3	0.3
S	0.2	–	–	–

^a By difference.

Table 2

Contents of fiber components in xylan, cellulose, ADF and pine wood (wt.-%-dry biomass samples).

	NDS	Hemicelluloses	Cellulose	Lignin	Silicate
Xylan	100.0	0.0	0.0	0.0	0.0
Cellulose	0.0	0.3	99.7	0.0	0.0
ADF	0.0	0.0	65.7	34.1	0.2
Pine wood	15.5	10.5	48.6	25.3	0.1

(NDF). Meanwhile, another segment of biomass sample is dissolved in an acid detergent (2% cetyl trimethyl ammonium bromide) under refluxing to remove both NDS and hemicellulose, and the insoluble remainder is termed acid detergent fiber (ADF), which contains cellulose, lignin and silicate. The ADF sample used in this study was obtained from the pine wood sample in this way. The content of hemicellulose in biomass sample can consequently result from the difference between the content of NDF and that of ADF. ADF is then dissolved with an aqueous solution of 72% H_2SO_4 at 20 °C for 3 h to eliminate cellulose, resulting in a sulfuric-acid-insoluble fiber (SIF). Finally, the contents of individual lignin and silicate are determined by the ignition of SIF.

2.3. Pyrolysis and analysis methods

Pyrolysis was carried out on a tubular stainless steel reactor which was vertically mounted. The schematic diagram of the apparatus was illustrated elsewhere (Wang et al., 2009). In each run, a 2.2 g sample of biomass was held in a stainless steel wire-mesh wrap and then placed in a flat-temperature zone of the reactor. Biomass pyrolysis started in a stream of argon by electric heating from room temperature to the predetermined temperatures with a heating rate of 10 °C/min, and held at the final temperature for 5 min. The pyrolysis temperature was measured by a thermocouple whose tip was forced to contact the sample wrap. The argon gas from the cylinder was dehumidified by a molecule sieve adsorber before the gas flowed into the reactor. The flow rate of argon was controlled accurately by the mass flow meter to be 200 ± 2 ml/min. The liquid product was captured in two series ice/water-cooled traps. The non-condensable gas was collected in a succession of gas bags at a temperature interval of 50 °C before the final temperature was reached. A final gas bag was used to collect the gas released in the isothermal stage (5 min). The char product was recovered after the sample was cooled down by power-off but keeping the stream of argon through the sample.

The four major gases (H_2 , CO, CH_4 and CO_2) was quantitatively determined using a gas chromatograph (Agilent 6820) equipped with a thermal conduct detector (TCD). Other light hydrocarbon gases such as C_2H_4 , C_2H_6 and C_3H_8 were not detected because these gases were reported to be minor (Xin et al., 2013). The overall gas yield referred to the summative yields of four main gases through an entire course of pyrolysis at each of the predetermined pyrolysis temperatures. The yield of liquid product was determined by weighing the traps before and after experiment. To detect the compounds in liquid product, the traps were carefully washed with acetone to dissolve out the liquid product. The water contents in the liquid products were determined using a Coulometry trace moisture analyzer (Mettler Toledo, C20). The compounds in the liquid product were firstly characterized by gas chromatograph mass spectrometry (GC–MS, PerkinElmer clams 500). The quantitative determination of typical compounds including acetic acid, 2-furfural, 2-furanmethanol, guaiacol, levoglucosan, phenol, toluene, m-xylene was carried out on a GC–FID analyzer (Haixin GC) equipped with a HP-5 capillary column, using the standard solutions of these compounds for calibration. Other compounds assigned by GC–MS were then determined in terms of the theoretic

relative molar response factors. The char yield was determined by weighing the solid sample before and after experiment. The char sample was stored in a desiccator for compositional analyses.

For comparison, the pyrolysis of four biomass samples was also conducted on a thermogravimetric analyzer (Mettler Toledo, TGA/SDTA851e). In this experiment, a 20 mg sample was held in a platinum crucible and heated to 700 °C under argon with a heating rate of 10 °C/min. The data on the mass loss as a function of temperature and the derivative mass loss with time (i.e., the rate of mass loss) were automatically recorded in an accessory computer. Unless stated otherwise, however, the pyrolysis data presented throughout the study refer to those obtained on the fixed bed reactor.

3. Results and discussion

3.1. Overall distributions of products

Since TG is widely used as a tool for biomass pyrolysis (Huang et al., 2012; Yang et al., 2007), the TG curves of the four samples are shown in Fig. 1 to assure the pyrolysis characteristics of the four samples. As expected, xylan was less stable. Its mass loss started at 220 °C and virtually finished at 350 °C. Cellulose was not decomposed at all in a common temperature range used for biomass torrefaction (200–300 °C), while the intense decomposition happened in the temperature range of 300–375 °C. ADF showed a similar profile of mass loss rate with cellulose, but the slight mass loss appearing in the temperature range of 200–300 °C indicated the occurrence of lignin decomposition at low temperature (Stefanidis et al., 2014). The char yields obtained at 700 °C were 16.7%, 16.1%, 18.6% and 20.3%, respectively, for xylan, cellulose, ADF and pine wood. This result was in agreement with the observation that lignin was more productive of char (Cao et al., 2014). However, the char yield of cellulose was much higher than that of 6.7% obtained by Yang et al. (2007), although the cellulose samples used in our and their studies were purchased from the same company.

The pyrolysis of pine wood reflected the superimposed pyrolysis characteristics of the main components. The decomposition of

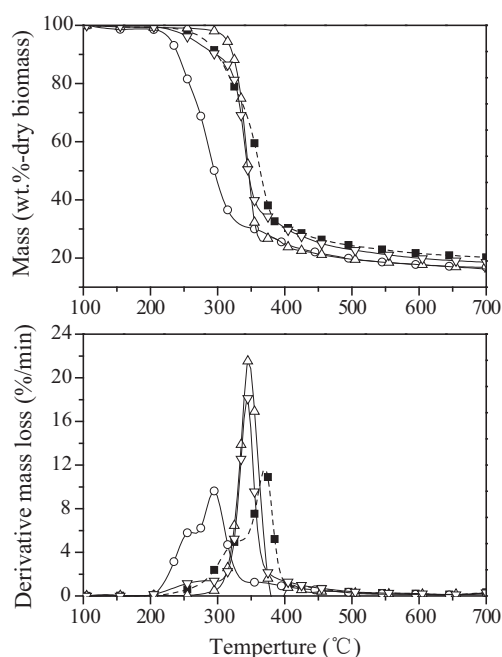


Fig. 1. The TG analyses of four biomass samples. ○, xylan; △, cellulose; ▽, ADF; ■, pine wood.

pine wood occurred in the temperature range of 200–300 °C. Above 300 °C, the inflected upcurve was implicative of the simultaneous decomposition of hemicellulose and cellulose. Compared to xylan, cellulose and ADF, however, pine wood showed the retarded mass loss till 400 °C, implying some interaction occurring between the components in pine wood.

The yields of three-phase products produced by the pyrolysis of the four samples at different temperatures in the fixed bed reactor are shown in Fig. 2, where the gas yield is the summative yield of four main gases (CO_2 , CO , CH_4 and H_2), and the liquid yield includes the oily product and water. It should be mentioned that all the pyrolysis experiments were done at least in duplicate, and the repetitive experiments showed the absolute errors were $\pm 0.3\%$, $\pm 0.8\%$, and $\pm 0.3\%$, respectively, for the yields of gaseous product, liquid product, and char product. It could be seen that xylan devolatilized to a large degree at 260 °C, whereas cellulose remained almost intact below 300 °C. These results were consistent with the TG observations. The char yields obtained at 350 °C were 23.2%, 24.7%, 34.8% and 38.6%, respectively, for xylan, cellulose, ADF and pine wood, with the gas yields of 5.8%, 0.1%, 2.2% and 6.1%, respectively. It was clear that at this temperature, the dominant decomposition product from cellulose was the liquid product with little gas product, and the gas production from pine wood resulted mainly from hemicellulose and NDS. Below 400 °C, the mass balances from the three-phase products collected were poorer, particularly for xylan and cellulose. In this case, it was visually observed that some tarry product was severely adhered on the colder part of the reactor wall. However, all the mass closures became better than 90% at temperatures higher than 500 °C. At 700 °C, all the mass closures were better than 96%. The char yields obtained at 700 °C were 17.2%, 16.9%, 21.0% and 22.3%, respectively, for xylan, cellulose, ADF and pine wood. Compared to the TG results, the char yields of xylan and cellulose obtained by two pyrolysis approaches were intimately close to each other, whereas for ADF and pine wood, the char yields obtained on the fixed bed reactor were, respectively, 2.4 and 2.1 percent higher than the corresponding TG results. This could be explained by the somewhat intensified componential interaction in the fixed bed reactor leading to an enhancement of the char deposit for ADF and pine wood but not for xylan and cellulose. With respect to the liquid yield, xylan had the highest liquid yield of 65.5% at 700 °C, followed by 63.3% for pine wood, 63.2% for cellulose, and 58.0% for ADF. It should be kept in mind that these liquid products included water.

3.2. Characterization of char

Fig. 3 shows the H/C atomic ratios and O/C atomic ratios in the chars obtained by the pyrolysis of the four samples at different temperatures. Xylan and cellulose had higher H/C and O/C ratios than ADF and pine wood. Xylan showed a marked decrease in both

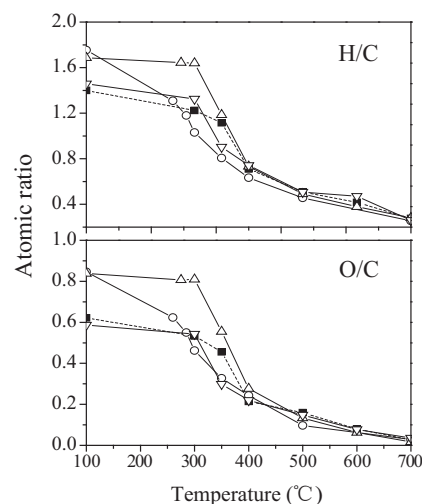


Fig. 3. Changes of H/C and O/C atomic ratios with pyrolysis temperature for four biomass samples. ○, xylan; △, cellulose; ▽, ADF; ■, pine wood.

the H/C ratio and the O/C ratio at 260 °C. Cellulose remained almost unchanged in the H/C and O/C ratios until 300 °C, but the noticeable reduction occurred above 300 °C. These results of xylan and cellulose were well consistent with the observations in Fig. 2. Further calculation demonstrated that for xylan, the difference value of H/C ratio (Dv-H/C) between 100 °C and 260 °C was perfectly twofold as much as that of O/C ratio (Dv-O/C), indicating that the dehydration was a predominant process in this temperature range; from 260 °C to 300 °C, the ratio of the Dv-H/C to the Dv-O/C fell to 1.7, implying the reactions of decarboxylation and dehydroxylation happening. For cellulose, the Dv-H/C between 300 °C and 350 °C was 1.8 times as much as the Dv-O/C , whereas from 350 °C to 400 °C, the ratio of Dv-H/C to the Dv-O/C decreased to 1.6 in connection with the violent release of CO and CO_2 (Fig. 5). For ADF, a slight decline in both the H/C ratio and the O/C ratio occurred at 300 °C, differing from cellulose but in line with the low-temperature decomposition of lignin as observed in Fig. 2. For pine wood, the decreases in the H/C and O/C ratios at 300 °C were reasonably in between as compared to xylan and ADF. A subtle observation was a slower change in the H/C and O/C ratios from 300 °C to 350 °C for pine wood by contrast to the results for the other three samples. This result, corresponding to a higher yield of char in this temperature range (Fig. 2), was attributed to the component interactions. This postulation might also be justified by the finding by Elyounssi et al. (2012) that a two-step pyrolysis, which included the isothermal pyrolysis at 360 °C and the subsequent rapid pyrolysis at a high temperature, enhanced the production of charcoal from eucalyptus wood but not from cellulose and

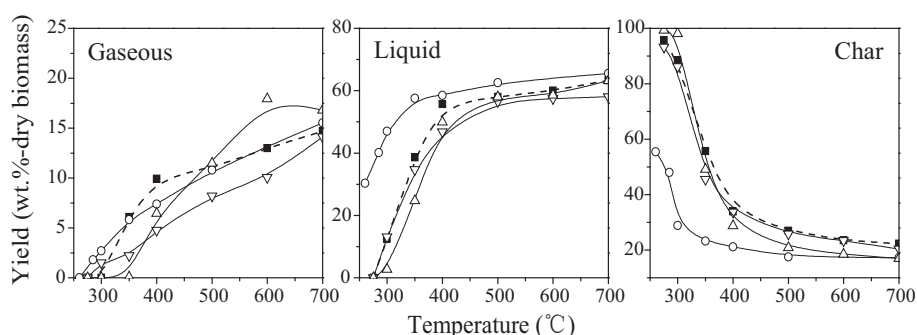


Fig. 2. The yields of gaseous, liquid and char products (wt.-%-dry biomass). ○, xylan; △, cellulose; ▽, ADF; ■, pine wood.

xylan. Finally from Fig. 3, it could be seen that at 700 °C, the elemental compositions of the chars approached each other.

To better understand the transformation of biomass components during pyrolysis, we used the biomass component determination method to analyze varying chars. As described in Section 2.2, this method classifies the organic entity of biomass into the four components, NDS (soluble in the neutral detergent solution), hemicellulose (soluble in the dilute hydrochloric acid but insoluble in the neutral detergent solution), cellulose (soluble in the concentrated sulfuric acid), and lignin (insoluble). It should be emphasized that each specific component in a char sample is possible to include the undecomposed residue of this component in biomass and a newly formed component as such. But the chemical structure of the latter may not be the same as that of the former. For example, the “lignin” component in a char sample is supposed to be a residue degraded from the realistic lignin in biomass together with an insoluble char deposited from the decomposition of non-ligninic components. In this case, the assigned component, lignin, is put in inverted commas to mean something special.

The changes of the four components with pyrolysis temperature for the four samples are shown in Fig. 4. As stated in Section 2.1, xylan was entirely soluble in the neutral detergent solution like NDS, while the char derived from xylan at 275 °C contained 44% of “lignin” and some portions of “hemicellulose” and “cellulose”, indicating that xylan was extensively decomposed, resulting in a quite inhomogeneous char at this temperature. From 275 °C to 400 °C, the content of “lignin” in the xylan-derived char increased dramatically. At 700 °C, the “lignin” component accounted for over 95% of the char, with a small portion of “cellulose” being present together.

Corresponding to a slight mass loss and scarcely any gas release of cellulose at 300 °C (Fig. 2), it was seen from Fig. 4 that the component of the char sample obtained from cellulose at this temperature did remain principally as cellulose. But some “hemicellulose” constituent was derived at this temperature. From 300 °C to 350 °C, the “hemicellulose” component increased to a maximum content in the char, along with the significant decomposition of cellulose to form liquid product but little gaseous product (Fig. 2). It is known that cellulose is initially decomposed to “active cellulose”, with little formation of light gases (Brandbury et al.,

1979; Pasangulapati et al., 2012). It was consequently postulated that the “hemicellulose” characterized in the cellulose-derived char might be related to the “active cellulose”. This “hemicellulose” constituent then decreased with temperature increasing. At 700 °C, the cellulose-derived char became entirely insoluble. For ADF, a similar result was observed on the formation of the “hemicellulose” component. A difference was that the “hemicellulose” component disappeared at 500 °C for ADF whereas it persisted at this temperature for cellulose. At 700 °C, ADF produced a completely insoluble char or a single “lignin” component, similar to cellulose.

For pine wood, the contents of NDS and hemicellulose in the char obtained at 300 °C were lower than those in the original sample, whereas the contents of cellulose and lignin became higher. It was firmly evident that the decomposition of pine wood at 300 °C was predominantly due to the decomposition of NDS and hemicellulose. At this temperature, an increase in the content of cellulose was partially attributed to the transformation of some NDS to “cellulose”. The change in the content of lignin was traded off by two opposite effects, the lignin decomposition and the conversion of NDS and hemicellulose to “lignin”. From 300 °C to 400 °C, the content of “lignin” appreciably increased as a result of the char formation arising from the cellulose decomposition. An interesting observation was that the chars obtained from pine wood in the temperature range of 600–700 °C still contained a distinct portion of “NDS” and “cellulose”. In contrast, “NDS” was no longer present for all other three samples, and “cellulose” existed only in a small amount for xylan but not at all for cellulose and ADF in this temperature range. It was clear that the char derived from pine wood at 700 °C was more inhomogeneous, although it had the elemental compositions close to those from the other three samples (Fig. 3).

3.3. Release rates and yields of gaseous products

The gas production characteristics of individual components have been extensively researched (Shen and Gu (2009); Yang et al., 2007). This work was intended to focus on a comparison of pine wood with xylan, cellulose and ADF in this regard. The release rates of four main gases with pyrolysis temperature are shown in Fig. 5. CO₂ and CO started to evolve from either xylan or ADF at

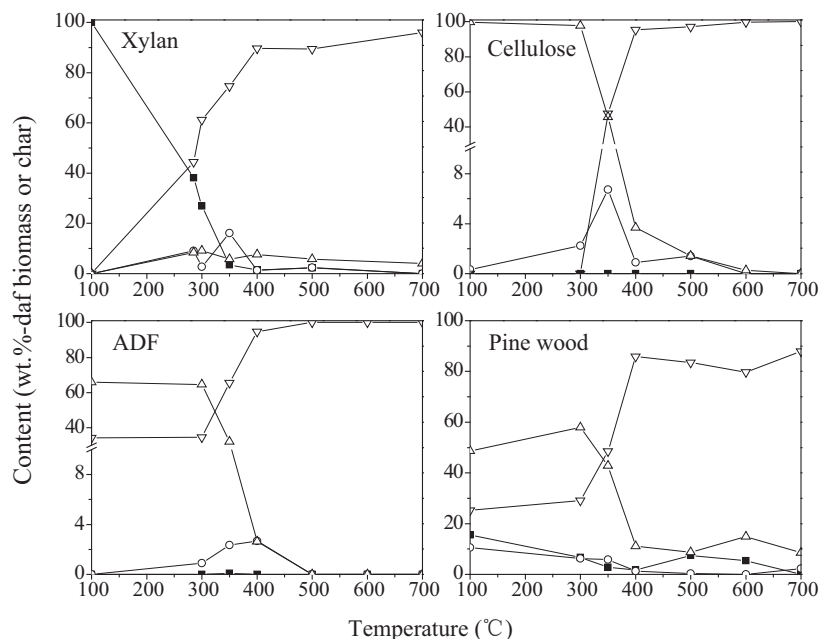


Fig. 4. The contents of NDS (■), hemicelluloses (○), cellulose (△) and lignin (▽) in raw biomass and chars obtained at varying pyrolysis temperatures.

275 °C. The formation of CO₂ and CO from pine wood in the initial stage could be attributed to the easy decomposition of NDS/hemicellulose and lignin. The release rate patterns of both CO₂ and CO above 350 °C for pine wood were quite similar to the corresponding patterns for ADF. The formation of CO₂ and CO from cellulose was not significant until the temperature was elevated above 375 °C, despite the significant decomposition of cellulose at 350 °C. The maximal release rate of CO₂ and CO appeared at a higher temperature for cellulose than did for pine wood and ADF. It was indicated that CO₂ and CO were generated by the subsequent reactions of the “hemicellulose” component and liquid product when the temperature increased above 375 °C. From the results of ADF and pine wood, it could be inferred that the release of CO₂ and CO was facilitated by the interactions between cellulose and lignin. For pine wood, the interactions might also be participated by NDS and hemicellulose, resulting in the retarded mass loss (Fig. 1), a higher yield of char (Figs. 2 and 3) and the increased heterogeneity of char (Fig. 4).

The release of CH₄ from xylan and cellulose commenced at the temperatures higher than 400 °C, where both xylan and cellulose underwent the extensive decomposition (Fig. 4). This meant that CH₄ did not form directly from xylan and cellulose but from the intermediates, similar to the process of CO₂ and CO formation from cellulose. An interesting observation from Fig. 5 was that the pattern of CH₄ release rate for pine wood closely resembled that for ADF. Both pine wood and ADF liberated CH₄ significantly in the temperature range of 375–525 °C and exhibited a sharp peak of CH₄ release with a peak top at 475 °C, distinct from the patterns of xylan and cellulose. It was apparent that lignin was a main precursor for the CH₄ production in the initial stage. In the later stage, nevertheless, cellulose and hemicellulose became the important contributors to the CH₄ production. As for H₂, the significant production occurred at the temperatures higher than 500 °C for all four samples, except that pine wood had a unique and small release peak of H₂ in the neighboring of 425 °C. A surprise was that xylan persisted with a high release rate of H₂ from 500–700 °C as pine wood did, in contrast to cellulose. The cumulative yields of the main gases produced from the four samples at different temperatures are shown in Table 3. It could be seen that xylan was

not a bad source of H₂ and CH₄, differing from the result by Xin et al. (2013) but similar to that by Lv et al. (2013).

3.4. Main species of liquid products

The yields of water and bio-oil in the liquid products produced separately from xylan, cellulose, ADF and pine wood are shown in Table 4, where the yields of bio-oil are obtained in terms of the differences between the total liquid yields and the water yields. It was seen that the liquid product produced from xylan embraced the highest content of water, despite the highest yield of liquid product. In contrast, ADF generated a higher yield of bio-oil than xylan and cellulose, indicating that lignin was not only a good precursor of char but also bio-oil. Pine wood exhibited an even higher yield of bio-oil than ADF. Wang et al. (2011) reported that the mixing of three components led to a decline in the yield of liquid product. Despite no detection of water in their work, an increase in the yield of gaseous product hinted a decreasing trend in the yield of bio-oil by the component-interactive effect. Stefanidis et al. (2014) found that the mixing of xylan, cellulose and lignin lowered the biomass yield in the fast pyrolysis. It appeared that the highest yield of bio-oil produced from pine wood was attributable to the presence of extractives in pine wood.

In the light of few reports on the elemental compositions of bio-oils, we tried to estimate the elemental compositions of the four bio-oils according to the differences in the amounts of C, H, and O elements between the raw sample and the sum of the gaseous and solid products, and the results are shown in Table 4. It could be seen that the bio-oils produced from xylan and cellulose were highly oxygenated, with the O/H atomic ratios of 0.32–0.33, while the ADF-derived bio-oil had a low O/H atomic ratio of 0.25, implying that the lignin-derived bio-oil was less oxygenated. Another plausible reason was that lignin promoted the formation of CO₂ and CO at lower temperature (Fig. 5) and could consequently inhibit the escape of highly oxygenated volatiles from cellulose. It was reasonable that the O/H atomic ratio for the pine wood-derived bio-oil was in between.

The compounds in bio-oil are widely characterized by GC–MS (Cao et al., 2014; Wang et al., 2009). For brevity, the compounds

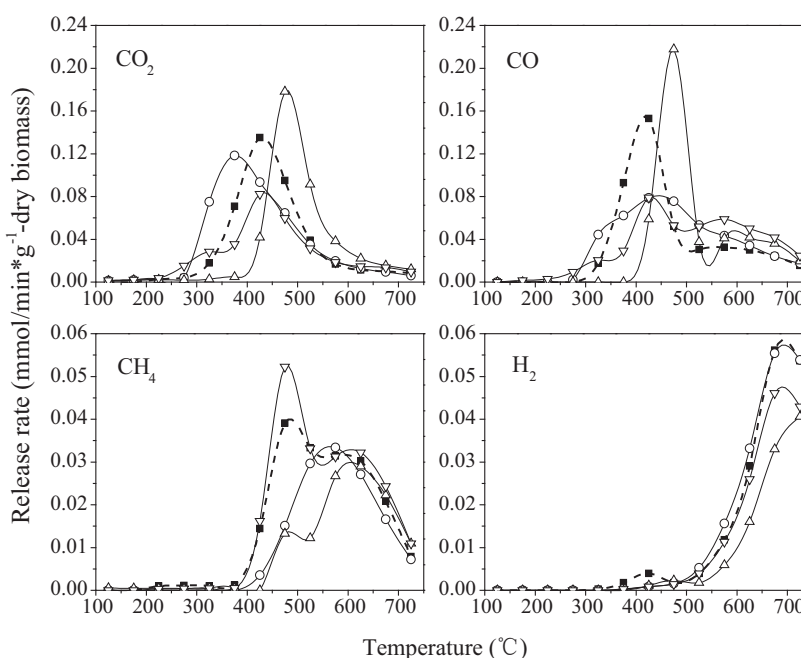


Fig. 5. The release rates of major gases from xylan (○), cellulose (△), ADF (▽) and pine wood (■) at varying pyrolysis temperatures.

Table 3
Cumulative yields of gases at different temperatures (mmol/g-dry biomass).

	T (°C)	CO ₂	CO	CH ₄	H ₂
Xylan	300	0.33	0.18	0.00	0.00
	500	1.70	1.38	0.22	0.04
	700	1.94	1.97	0.64	0.82
Cellulose	300	0.04	0.00	0.01	0.00
	500	1.47	1.42	0.13	0.02
	700	1.90	2.09	0.56	0.49
ADF	300	0.20	0.13	0.00	0.00
	500	1.13	1.09	0.47	0.03
	700	1.41	1.96	0.96	0.66
Pine wood	300	0.10	0.07	0.01	0.00
	500	1.59	1.50	0.41	0.05
	700	1.82	2.00	0.85	0.79

Table 4
The yield of water, bio-oil (wt.-%-dry biomass) as well as the average compositional formula of bio-oil at the pyrolysis temperature of 700 °C.

	Xylan	Cellulose	ADF	Pine wood
Water yield	34.1(±1.0)	32.7(±1.0)	23.3(±0.7)	24.9(±0.6)
Bio-oil yield ^a	31.4	30.5	35.0	38.6
Formula of bio-oil	CH _{1.06} O _{0.34}	CH _{1.04} O _{0.34}	CH _{1.24} O _{0.31}	CH _{1.07} O _{0.31}

^a Calculated by the difference between liquid yield and water yield.

in the four bio-oils determined by GC–MS are grouped into ten categories including acids, alcohols, aldehydes, esters, furans, ketones, guaiacols, phenols, sugars, and others. The yields of these groups of compounds are shown in Fig. 6. Pine wood and xylan had higher yields of acids than cellulose and ADF, probably because the former two samples originally contained some acidic monomers. Xylan had a dramatically high yield of furans, in which the yields of 2-furfural and 2-furanmethanol reached as high as 11.7% (not shown). Cellulose generated furans in a relatively small amount. This could account for a higher yield of furans from pine wood than from cellulose and ADF. As for sugars, little was formed from xylan, whereas cellulose had a total sugar yield of 2.6%, in which the yields of levoglucosan and D-allose were respectively 0.7% and 0.2% (not shown). This yield of levoglucosan from cellulose was unexpectedly low because the content of levoglucosan in the bio-oil was reported to be as high as 20–60% by weight at low temper-

ature (Brandbury et al., 1979; Shen et al., 2010). D-allose and levoglucosan were also assigned to be the product from ADF and pine wood. However, the liquid product from pine wood contained a series of saccharide including D-manosan, D-galactosan, D-talopyranose and methyl-2,6-anhydro-α-D-altroside (not shown), whereas none of these compounds was observed for xylan, cellulose and ADF. Guaiacols were indeed the product of ADF and pine wood rather than xylan and cellulose. It was noteworthy that the total yield of the detected compounds from cellulose was much lower than that of bio-oil; compared to cellulose, ADF had relatively a high total yield of the detected compounds, with the high yields of aldehydes and ketones. It was suggested that the pyrolysis of pure cellulose might form some large molecular weight compounds as volatile matter, which could not be detected by GC–MS; the co-existence of cellulose and lignin facilitated the cleavage of the volatile matter to smaller molecular weight compounds. Pine wood had not only a highest total yield of the detected compounds (17.7%) but also the richest varieties of compounds. This could be attributed to the more complex mixture of components in pine wood and the interactive reactions between different components as well.

4. Conclusions

This comparative study revealed the complex interactions occurring between different components in pine wood during the pyrolysis. The componential interactions led to the faster release of CO₂ and CO, the retarded mass loss, a higher yield of char, and the increased heterogeneity of char. Pine wood had the highest yield of bio-oil (excluding water) among the four biomass samples. The pine wood-derived bio-oil contained the richest varieties of compounds detected by GC–MS. The compositional formula of the pine wood-derived bio-oil was estimated to be CH_{1.07}O_{0.31} against CH_{1.06}O_{0.34}, CH_{1.04}O_{0.34} and CH_{1.24}O_{0.31} for the bio-oils, respectively, derived from xylan, cellulose and ADF.

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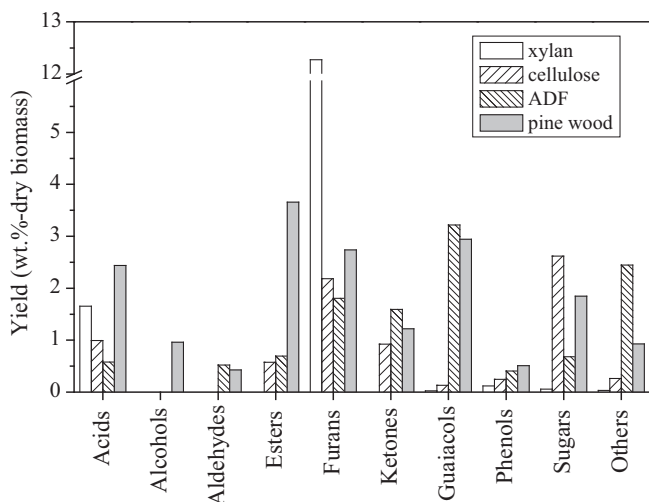


Fig. 6. Distributions of different groups of liquid compounds produced from four biomass samples at 700 °C.

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